

Full length article

# Effect of single $\text{Si}_{1-x}\text{C}_x$ coating and compound coatings on the thermal conductivity and corrosion resistance of Mg–3Sn alloy

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## Abstract

A single  $\text{Si}_{1-x}\text{C}_x$  coating and compound coatings were deposited on Mg–3Sn matrix alloy by magnetron sputtering method. Compound coatings included Mg or Mg/AlTi intermediates between Mg–3Sn substrate and  $\text{Si}_{1-x}\text{C}_x$  coating. The thermal conductivity of the Mg–3Sn alloy after coating was enhanced at room temperature. The results showed that the Mg–3Sn alloy coated with Mg/AlTi/ $\text{Si}_{1-x}\text{C}_x$  displayed higher thermal conductivity, its thermal conductivity after corrosion was 90.1 W/(m K) and 108.4 W/(m K) at 25 °C and 100 °C, respectively. Meanwhile, it was revealed that the Mg/ $\text{Si}_{1-x}\text{C}_x$  and Mg/AlTi/ $\text{Si}_{1-x}\text{C}_x$  compound coatings had nobler  $E_{\text{corr}}$  and much lower  $i_{\text{corr}}$ , higher  $R_p$ , compared with the bare Mg–3Sn and Mg–3Sn/ $\text{Si}_{1-x}\text{C}_x$  system, and improved the corrosion resistance of the magnesium substrate. Copyright 2015, National Engineering Research Center for Magnesium Alloys of China, Chongqing University. Production and hosting by Elsevier B.V. All rights reserved.

**Keywords:**  $\text{Si}_{1-x}\text{C}_x$  coating; Compound coatings; Thermal conductivity; Corrosion resistance

## 1. Introduction

Magnesium alloys are potential heat dissipation materials for their suitable mechanical properties, electromagnetic shielding performance, light weight and high thermal conductivity. However, the low corrosion resistance of magnesium alloys limits their practical applications in humid environment. In order to protect magnesium alloys from corrosion, many surface treatments for magnesium alloys were provided [1–7]. The corrosion resistance and tribological property of the coatings for magnesium alloys were fully studied. However, few papers concerned about thermal properties [8], especially the high heat transfer characteristic. It is well-known that pure magnesium possesses a high thermal conductivity of 156 W/

m K at room temperature. However, the magnesium alloys are easily to be corroded in wet environment, causing some products, such as  $\text{Mg}(\text{OH})_2$  (4.5 W/m K), MgO (36 W/m K),  $\text{SnO}_2$  (40 W/m K) [9–12]. These corrosion products cover the surface of magnesium alloys, forming a barrier layer to lower the heat-conducting property. Therefore, it is necessary to study on thermal conductivity of coated magnesium alloy or search for high heat-conducting coatings.

SiC is well known for the high thermal conductivity and electrical resistivity, good corrosion resistance and optical performance, it may counterbalances the disadvantages of magnesium alloy by depositing SiC film on magnesium alloys. J. S. Goela et al. [13] reported the thermal conductivity of CVD-SiC reached up to 300–374 W/m K at room temperature. To maintain or improve the thermal conductivity of magnesium alloys used in severe environment, a high heat-conducted SiC film was deposited on Mg–3Sn alloy by RF magnetron sputtering in this work. Nevertheless, adhesion between ceramic film and metallic substrate was poor due to

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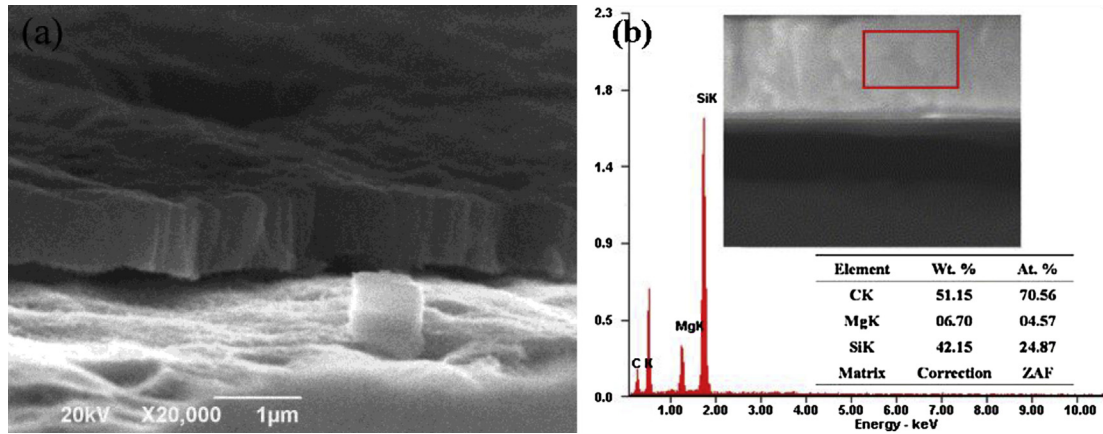


Fig. 1. The cross section SEM micrograph and EDS result of Si<sub>1-x</sub>C<sub>x</sub> film deposited on the Mg-3Sn substrate.

their different structure, elastic modulus and line-expansion coefficient [14]. And the poor adhesion performance may decrease the thermal conductivity of coated magnesium alloy. In order to enhance the adhesion performance between Mg-3Sn substrate and SiC ceramic film and understand the effect of intermediate between top ceramic coating and magnesium alloy substrate on the thermal conductivity of coated magnesium alloy, a intermediate of Mg and AlTi was produced.

## 2. Experimental details

As-cast Mg-3Sn alloy (10 mm × 10 mm) which contain 3 wt. % Sn was used as substrate in this study. Before sputtering, the polished samples were ultrasonic cleaning in acetone and alcohol for 5 min, respectively, and dried in warm air. All films were deposited using RF magnetron sputtering method. A SiC, Mg and TiAl target were used for top Si<sub>1-x</sub>C<sub>x</sub> ceramic film and intermediate layers. The sputtering time was

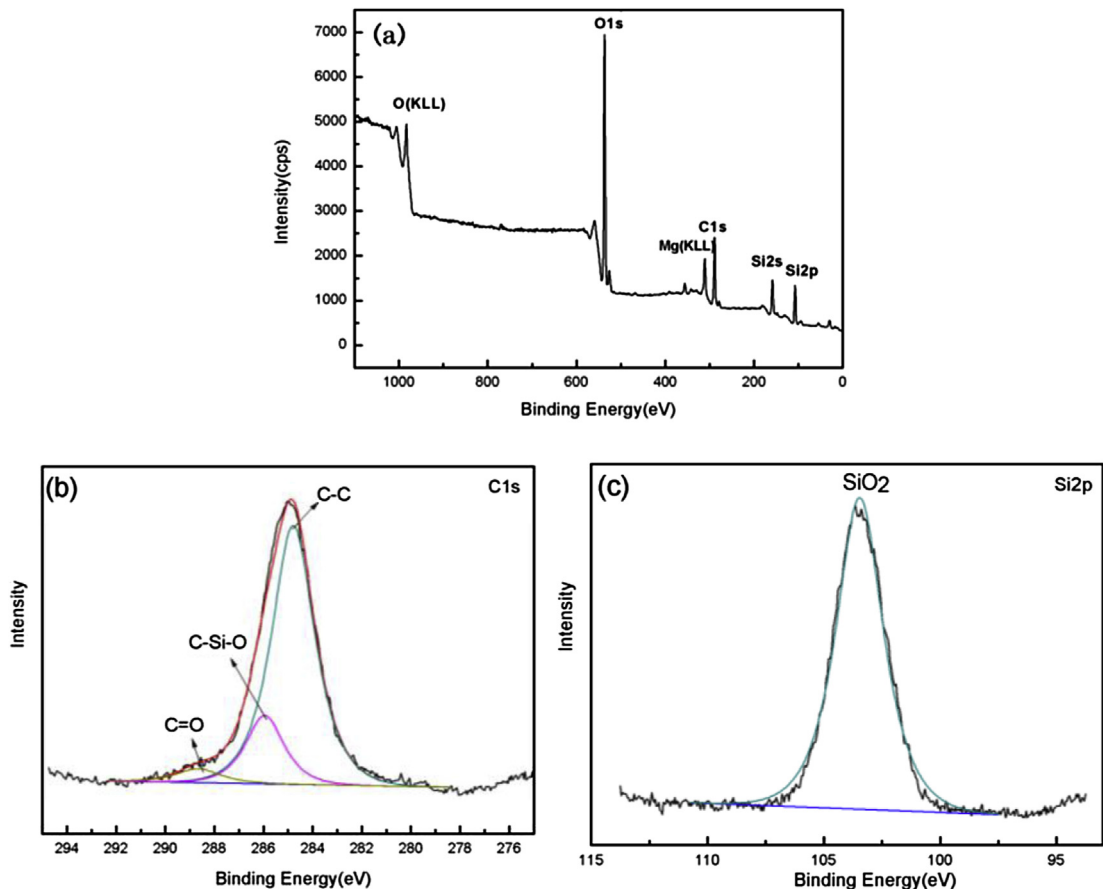


Fig. 2. XPS spectra of Si<sub>1-x</sub>C<sub>x</sub> film (a) on Mg-3Sn substrate and C1s (b) and Si2p (c) XPS region scan patterns.

2.5 h for each layer. The films were deposited using the following process parameters: base pressure is  $4.2 \times 10^{-3}$  Pa, gas pressure is 1.5 Pa, RF power is 200 W, substrate temperature is 180 °C.

The microstructure and chemical analyses of the sputtered film were performed using a scanning electron microscopy (SEM) with an energy dispersive spectrometer (EDS). The chemical bindings within the  $\text{Si}_{1-x}\text{C}_x$  film were employed using X-ray photoelectron spectroscopy (XPS) with a monochromatic  $\text{AlK}\alpha$  (1486.6 eV) line of an X-ray source, and the measurements were taken in an ultra-high vacuum environment. Binding energy positions were verified using the C 1s peak at 284.8 eV, which was associated to C–C and/or C–H bindings. The peaks were adjusted using Gaussian curves and the background was determined by the Shirley method. Besides, the thermal conductivity measurements of bare or coated magnesium alloy before and after salt spray test were performed with a NETZSCH model LFA447 Flash Analyzer. In order to research the difference of thermal conductivity between bare and coated magnesium alloys and the changes of thermal conductivity in different corrosion condition and temperatures. The bare and coated magnesium alloy samples were made into  $\Phi 12.9 \text{ mm} \times 2.9 \text{ mm}$ , and some of them (exposure area:  $\Phi 12.9 \text{ mm}$ ) were corroded for 4 days using salt spray test in intermittent hand spraying model (Spray 2 h;

Pause 22 h). The thermal conductivity of samples was measured at 25 °C and 100 °C, respectively. In addition, potentialdynamic polarization experiments were done using an EG&G potentiostat model 2273. Three-electrode system was used with the samples as working electrode, platinum as counter electrode and saturated calomel electrode (SCE) as reference electrode. Work electrodes were embedded into epoxy resin with an exposure area of  $10 \text{ mm} \times 10 \text{ mm}$ , the scan rate for potentiodynamic polarization curves was 1 mV/s. The corrosive medium for salt spray test and polarization experiments was 5 wt. % and 3.5 wt. % NaCl solution (analytical reagent), respectively.

### 3. Results and discussion

#### 3.1. Characteristics of $\text{Si}_{1-x}\text{C}_x$ films and intermediate layers

Fig. 1 shows the cross section morphology (a) and EDS (b) result of  $\text{Si}_{1-x}\text{C}_x$  film directly deposited on the Mg–3Sn matrix. To get the cross section of  $\text{Si}_{1-x}\text{C}_x$  film, the sample was breaking off. As can be seen from Fig. 1(a), the cross section of  $\text{Si}_{1-x}\text{C}_x$  film is dense without any porous, and the coating's thickness is about 1  $\mu\text{m}$ . However, the adhesion between Mg–3Sn substrate and thin film is poor. The coating's

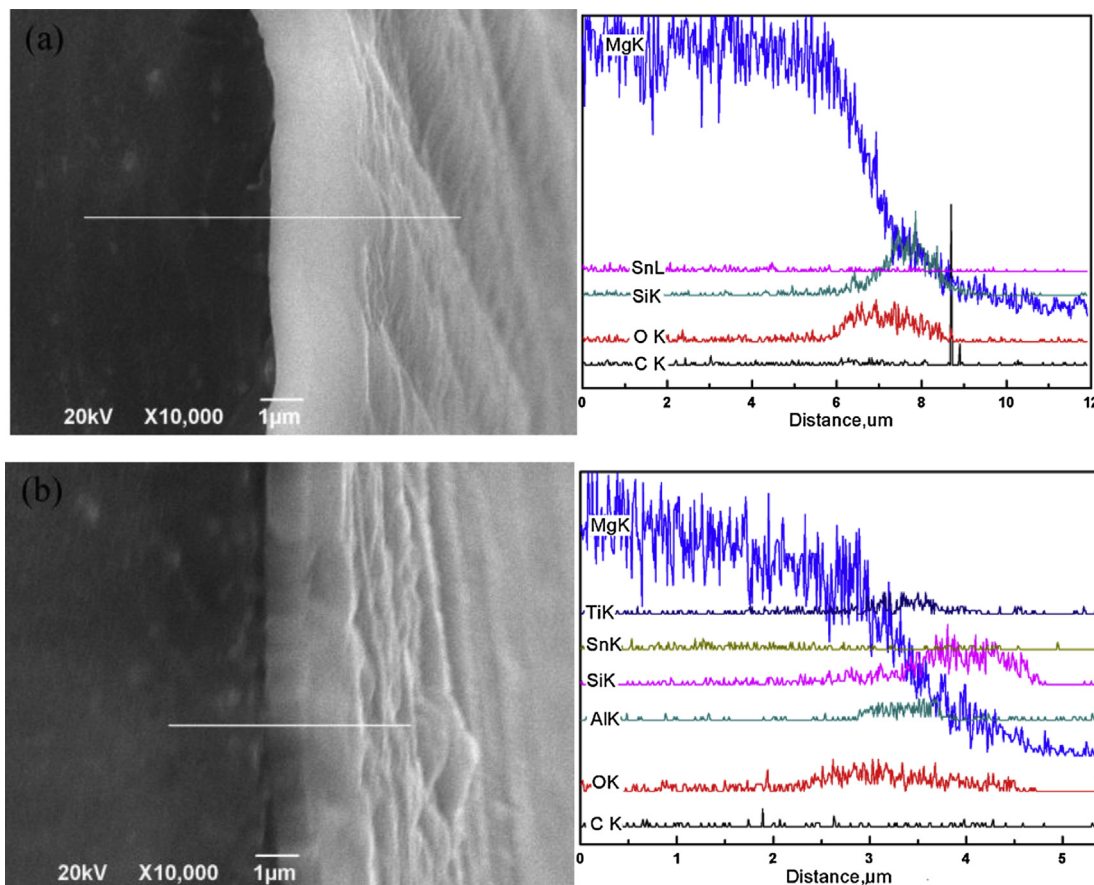


Fig. 3. Cross-sectional SEM images and EDS results of (a) Mg–3Sn/Mg/ $\text{Si}_{1-x}\text{C}_x$  and (b) Mg–3Sn/Mg/AlTi/ $\text{Si}_{1-x}\text{C}_x$  systems.

EDS result shows the film mainly contains C and Si apart from Mg element, and the atom quantity ration between C and Si is approximate 3:1.

The binding nature of the  $\text{Si}_{1-x}\text{C}_x$  film was investigated using XPS analysis. Fig. 2(a) shows the XPS spectra of the coating. It is found that the  $\text{Si}_{1-x}\text{C}_x$  film composed of C, Si, Mg and O. The element Mg in the film formed through the matrix diffusion. Besides, there is a high concentration of O content due to the formation of oxide on the active surface of  $\text{Si}_{1-x}\text{C}_x$  film after sputtering deposited. The C 1s spectra of the  $\text{Si}_{1-x}\text{C}_x$  film is presented in Fig. 2(b), three binding energy peaks of C 1s are 284.79 eV, 285.95 eV and 288.65 eV, corresponding to the one of C 1s in C–C, C–Si–O [15], and C=O [16] chemical bond, respectively. In this spectrum, the C–C binding predominated and this result expected these chemical bonding comprised major of amorphous carbon [16,17]. In addition, Fig. 2(c) shows the Si 2p spectrum, the only binding energy peak of Si 2p is 103.46 eV, corresponding to  $\text{SiO}_2$  formed when exposing in air. The XPS result shows the film contains C and Si, while there isn't crystal SiC formed in the film at the sputtering condition. Consequently, it is found that the  $\text{Si}_{1-x}\text{C}_x$  film is a rich carbon and amorphous structure film, which corresponds to the result of EDS in Fig. 1(b).

In order to improve the adhesion and corrosion resistance of coatings, Mg and AlTi intermediate layers were sputtering deposited on the Mg–3Sn substrates. As shown in Fig. 3(a), the Mg layer, as an interlayer, combined closely with Mg–3Sn substrate and  $\text{Si}_{1-x}\text{C}_x$  film. Especially, no obvious adhesion interface of between Mg intermediate and  $\text{Si}_{1-x}\text{C}_x$  film was observed while the difference of composition shown in EDS result can deduce the interface of them. And it means that there is a strong interface bonding. The relative EDS result shows us a gradual decline of Mg element at 6.2–8.5  $\mu\text{m}$  distance, and the Si element was arisen at 7–8.5  $\mu\text{m}$  while the O element was arisen at the range of 6.2–8.5  $\mu\text{m}$ . The thickness of total coating is about 2.3  $\mu\text{m}$ . Fig. 3(b) shows the cross section micrograph and EDS analysis result of Mg–3Sn/Mg/AlTi/ $\text{Si}_{1-x}\text{C}_x$  systems. The adhesion between substrate and coatings was improved and the interfaces of each coating were not clear. From relative EDS result, the Mg, Al, Ti, Si elements were found and changed gradually. The Si, O element was arisen at the range of 3.2–4.6  $\mu\text{m}$  and 2.1–4.6  $\mu\text{m}$ , respectively. The thickness of coating is about 2.5  $\mu\text{m}$ . It can be inferred that an element diffusion phenomenon occurred among the interfaces of coatings from Fig. 3. Meanwhile, it is found that the adhesion between compound coatings and Mg substrate is obviously improved, compared with the single  $\text{SiC}_x$  coating in Fig. 1.

### 3.2. The thermal conductivity of bare and coated magnesium alloys

Fig. 4(a) shows the thermal conductivities of Mg–3Sn alloy substrate and coated Mg–3Sn alloy with different films at 25 °C and 100 °C, respectively. The thermal conductivities of coated alloys are higher than that of bare alloy at 25 °C, however, the thermal conductivities decrease after coating

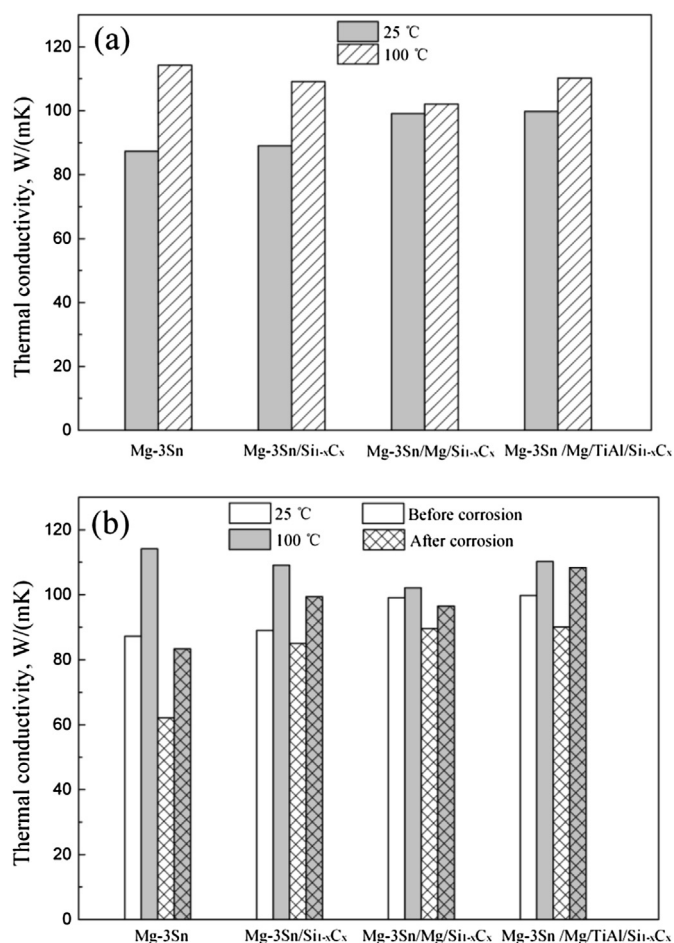


Fig. 4. Thermal conductivities of uncoated and coated Mg–3Sn alloys at different temperatures (a), before and after (b) corrosion.

single or compound films at 100 °C. The thermal conductivity of bare Mg–3Sn alloy is 87.3 W/(m K) at 25 °C, while the thermal conductivities of the coated magnesium alloys can reach to 89.0, 99.1, 99.8 W/(m K) after coating with  $\text{Si}_{1-x}\text{C}_x$

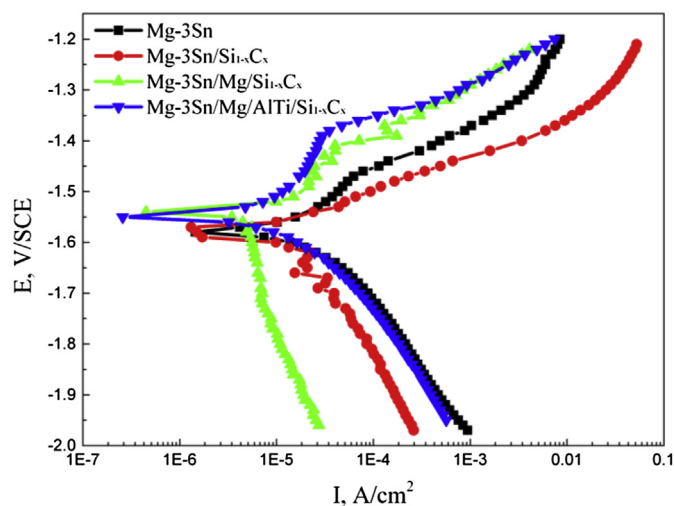


Fig. 5. Polarization of bare and coated magnesium alloys with different coatings.



Table 1

Fitting results of polarization curves of bare Mg–3Sn alloy substrate, different coatings systems in 3.5 wt. % NaCl solution.

|  | Sample |   |  |   |
|--|--------|---|--|---|
|  | Mg–3Sn | Mg–3Sn/Si <sub>1–x</sub> C <sub>x</sub> | Mg–3Sn/Mg/Si <sub>1–x</sub> C <sub>x</sub> | Mg–3Sn/Mg/AlTi/Si <sub>1–x</sub> C <sub>x</sub> |
| E <sub>corr</sub> , V                  | –1.58  | –1.57                                   | –1.54                                      | –1.55   |
| i <sub>corr</sub> , μA/cm <sup>2</sup> | 16.72  | 11.49                                   | 2.74                                       | 1.23  |
| R <sub>p</sub> , Ω cm <sup>2</sup>     | 1572   | 2833                                    | 34,061                                     | 45,145  |

film, Mg/Si<sub>1–x</sub>C<sub>x</sub> and Mg/AlTi/Si<sub>1–x</sub>C<sub>x</sub> compound films, respectively. Correspondingly, the thermal conductivities of uncoated and coated alloys are 114.2, 109.1, 102.1, 110.2 W/(m K) at higher temperature of 100 °C, respectively.

The heat-conducting ability of the Si<sub>1–x</sub>C<sub>x</sub> film or pure Mg, TiAl intermediates is higher than Mg–3Sn matrix, therefore the high thermal conductive coatings become a fast track which the quantity of heat can be quickly passed, and improve the thermal conductivities of coated alloys at room temperature. While the poor adhesion between magnesium alloy substrate and Si<sub>1–x</sub>C<sub>x</sub> film (Fig. 1(a)) and added interfaces impede the heat transfer strongly at higher temperature, leading to decrease thermal conductivities of coated alloys, consequently.

Fig. 4(b) shows the thermal conductivities of bare and coated Mg–3Sn alloys before and after salt spray test. In Fig. 4(b), it is found that the thermal conductivities reduced after salt spray test for 4 days, because of the formation of corrosion products with low thermal conductivity in samples. But all thermal conductivity values of coated magnesium alloys after corrosion are higher than that of uncoated alloy (62.1 W/(m K) at 25 °C and 83.4 W/(m K) at 100 °C), that is because the corrosion products of coating are different from uncoated Mg–3Sn alloy. Meanwhile, it also suggests that the more the quality of coating is, the better the thermal conductivity and corrosion resistance are. After corrosion, the thermal conductivity of magnesium alloy coated with Mg/TiAl/Si<sub>1–x</sub>C<sub>x</sub> coating is the highest, and reaches up to 90.1 W/(m K) at 25 °C and 108.4 W/(m K) at 100 °C, respectively.

### 3.3. Corrosion behaviors

The corrosion behaviors of Si<sub>1–x</sub>C<sub>x</sub> coatings are investigated by potentiodynamic curves. Fig. 5 shows the polarization of uncoated and coated Mg–3Sn alloy in 3.5 wt. % NaCl solution. It can be seen from Fig. 5 that the corrosion potential values of Mg–3Sn/Mg/Si<sub>1–x</sub>C<sub>x</sub> and Mg–3Sn/Mg/AlTi/Si<sub>1–x</sub>C<sub>x</sub> systems are obviously higher than that of Mg–3Sn/Si<sub>1–x</sub>C<sub>x</sub> system and Mg–3Sn alloy. For the bare Mg–3Sn alloy and Mg–3Sn/Si<sub>1–x</sub>C<sub>x</sub> system, an activation-controlled cathodic process occurs in the cathodic branch, and the main reaction is hydrogen evolution [12]. When the applied potential increases into the anodic branch, an activation-controlled anodic process is observed. The polarization current increased by increasing the applied anodic potential and the effect of the passivation is not obviously. But, for the Mg–3Sn/Mg/Si<sub>1–x</sub>C<sub>x</sub> and Mg–3Sn/Mg/AlTi/Si<sub>1–x</sub>C<sub>x</sub> systems, the phenomenon of clear passivation occurs in the anodic branch, and the passivation range reaches 100 and

200 mV, respectively. It is also explained that the compound coatings present an excellent corrosion resistance.

According to the polarization curves displayed in Fig. 5, electrochemical parameters including corrosion current density (i<sub>corr</sub>) and corrosion potential (E<sub>corr</sub>) calculated using Tafel extrapolation are summarized in Table 1. It is found that the E<sub>corr</sub> for coated magnesium alloys show a little positive shift than bare Mg–3Sn alloy, but the i<sub>corr</sub> arises varies remarkably with different coatings. The Mg/AlTi/Si<sub>1–x</sub>C<sub>x</sub> composite coatings exhibit the nobler E<sub>corr</sub> with a value of –1.55 V and the lowest i<sub>corr</sub> with a value of 1.23 μA cm<sup>–2</sup>, while bare substrate showed the lowest E<sub>corr</sub> with a value of –1.58 V and the highest i<sub>corr</sub> with a value of 16.72 μA cm<sup>–2</sup>. The values of polarization resistance (R<sub>p</sub>) calculate with the Stern–Geary formula, the corrosion resistance of Mg–3Sn/Mg/AlTi/Si<sub>1–x</sub>C<sub>x</sub> systems increases by nearly 30 times, compared with bare Mg–3Sn alloy.

However, corrosion potential value of Mg–3Sn/Si<sub>1–x</sub>C<sub>x</sub> sample is very close to the value of bare magnesium alloy due to the thinner coating's thickness of about 1–2.5 μm and the existence of the surface coating defects. In theory, ceramic coatings can separate the substrate from the aggressive environment and hence protect the substrate magnesium alloy. However, in reality, the formation of small structural defects in the coating-pinholes, pores, or cracks is almost impossible to avoid totally [18]. Every defect allowing corrosion medium to contact substrate surface leads to the formation of a galvanic cell, and pitting corrosion starts [19], and decreases the corrosion resistance of Si<sub>1–x</sub>C<sub>x</sub> film.

Therefore, from the analysis mentioned above, it can be seen that the Mg/Si<sub>1–x</sub>C<sub>x</sub> compound coatings and Mg/AlTi/Si<sub>1–x</sub>C<sub>x</sub> composite coatings both provided excellent protection for the bare substrate. The nobler E<sub>corr</sub> and much lower i<sub>corr</sub>, higher R<sub>p</sub> for the Mg/Si<sub>1–x</sub>C<sub>x</sub> and Mg/AlTi/Si<sub>1–x</sub>C<sub>x</sub> composite coatings indicate the better protection compared with the bare Mg–3Sn and Mg–3Sn/Si<sub>1–x</sub>C<sub>x</sub> system.

### 4. Conclusion

1. The structure of deposited Si<sub>1–x</sub>C<sub>x</sub> film is rich carbon and amorphous.
2. The thermal conductivities of coated Mg–3Sn alloy are higher matrix alloy at room temperature because the high thermal conductive coatings become a fast track which the quantity of heat can be quickly passed, and improve the thermal conductivities of coated alloys.
3. After corrosion, the compound coatings can protect Mg-alloy substrate from corrosion effectively, and the Mg/TiAl/Si<sub>1–x</sub>C<sub>x</sub> compound coating shows the highest heat-

conducting property at corrosion condition, and the values of thermal conductivity are reaching up to 90.1 W/(m K), 108.4 W/(m K) at 25 °C and 100 °C, respectively.

4. The compound coatings consisted of more coatings can improve the quality of coating, and have the nobler  $E_{\text{corr}}$  and much lower  $i_{\text{corr}}$ , higher  $R_p$ , compared with the bare Mg–3Sn and Mg–3Sn/Si<sub>1-x</sub>C<sub>x</sub> system. So the corrosion resistance is enhanced.

## References

- [1] Y.W. Song, D.Y. Shan, E.H. Han, *Electrochim. Acta* 53 (2008) 2135.
- [2] S.Y. Zhang, Q. Li, X.K. Yang, X.K. Zhong, Y. Dai, F. Luo, *Mater. Charact.* 6 (2010) 269.
- [3] T. Lei, C. Ouyang, W. Tang, L.F. Li, L.S. Zhou, *Surf. Coat. Technol.* 204 (2010) 3798.
- [4] A.L.K. Tan, A.M. Souter, I.F. Annergren, Y.N. Liu, *Surf. Coat. Technol.* 198 (2005) 478.
- [5] H. Pokhmurska, B. Wielage, T. Lampke, T. Grund, M. Student, N. Chervinska, *Surf. Coat. Technol.* 20 (2008) 4515.
- [6] C. Sella, J. Lecoeur, Y. Sampeur, P. Catania, *Surf. Coat. Technol.* 60 (1993) 577.
- [7] G.S. Wu, X.Q. Zeng, G.Y. Li, S.S. Yao, X.M. Wang, *Mater. Lett.* 60 (2006) 674.
- [8] J.A. Curran, T.W. Clyne, *Surf. Coat. Technol.* 199 (2005) 177.
- [9] W.M. Rohsenow, J.P. Hartnett, Y.I. Cho, *Handbook of Heat Transfer*, third ed., McGraw-Hill Professional, United States of America, 1998.
- [10] Z.X. Shi, *Effect of Inorganic Fillers on the Thermal Conductivity and Flame Resistance of Epoxy Resin*, Nanjing University of Aeronautics and Astronautics, Nanjing, 2011.
- [11] L. Gmelin, K. Kraut, A.N.F. Naumann, *Handbuch der Anorganischen Chemie*, Verlag Chemie, Berlin, 1967.
- [12] X.B. Liu, D.Y. Shan, Y.W. Song, R. S Chen, E.H. Han, *Electrochim. Acta* 56 (2011) 2582.
- [13] J.S. Goela, N.E. Brese, L.E. Burns, M.A. Pickering, *MRS Bull.* 26 (2001) 458.
- [14] M.F. Chen, D. B Liu, C. You, X.J. Yang, Z.D. Cui, *Surf. Coat. Technol.* 201 (2007) 5688.
- [15] Y. Zou, J.F. Du, H.Y. Dai, D. Ren, N.K. Huang, *Vacuum* 85 (2010) 26.
- [16] T. Maruyama, H. Bang, N. Fujita, Y. Kawamura, S. Naritsuka, M. Kusunoki, *Diam. Relat. Mater.* 16 (2007) 1078.
- [17] G. Capote, L.F. Bonetti, L.V. Santos, V.J. Trava-Airoldi, E.J. Corat, *Thin Solid Films* 516 (2008) 4011.
- [18] H. Altun, S. Sen, *Mater. Des.* 27 (2006) 1174.
- [19] F. Hollstein, R. Wiedemann, J. Scholz, *Surf. Coat. Technol.* 162 (2003) 261.